Electron Emission from Insulator and Semiconductor Surfaces by Multiphoton Excitation Below the Optical Damage Threshold

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ABSTRACT

Electron emission due to 1.06μ and 0.35μ laser excitation has been measured at several pulse lengths for a number of wide bandgap semiconductors and insulators. The dependence on fluence and wavelength are consistent with multiphoton excitation across the bandgap. The work functions of the materials investigated do not appear to influence the rate-limiting multiphoton excitation process.

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The physical processes accompanying the interaction of intense laser beams with surfaces have been the subject of much scientific and technological interest in recent years because of the importance of this topic to optical damage investigations and laser processing of materials. An effective probe of these physical processes is the emission of electrons, ions and neutral atoms due to intense laser excitation. Most of the previous work of this type has been performed with photon energies above or near the optical bandgap of the materials investigated, so that linear absorption plays the dominant role in the emission process. A few investigations have been performed with photon energies much smaller than the bandgap,[1] but they have not been done in ultra-high vacuum (UHV), and the results may therefore reflect the effects of adsorbed impurities. We report the first comprehensive study of multiphoton-induced photoemission in UHV conditions for a number of single-crystal, polycrystalline, and glassy optical materials with a large range of optical bandgaps. The behavior of the charged particle emission as a function of laser beam fluence for fixed pulse duration is suggestive of a multiphoton excitation across the bandgap. The dependence on laser pulsewidth in the range 1-30 nsec implies, however, that more complex mechanisms may also be involved.

The experiments have been carried out in a UHV system at $10^{-9} - 10^{-10}$ Torr. The sample is held in a grounded metal holder and is enclosed in a collector can, surrounded by an outer shield can, both of which are held at a common variable bias potential of up to ± 300 V. Holes in these cans allow entrance and exit of the laser beam. The time-integrated

charge accumulated on the collector can is measured with an electrometer. With this arrangement, the collector is shielded by the outer can from stray charges present in the vacuum system, and any photoemitted charge caused by scattered laser light impinging on the collector is merely recollected by its nearly closed surface. During the three minute interval between laser shots an ion pump is turned on in order to provide electrons and ions which return the target surface to its equilibrium potential. The target is illuminated by the 1.06μm fundamental and harmonics of a Nd laser capable of providing pulses of variable temporal width with flat tops and $\leq$ 0.5 nsec rise and fall times. The illuminated region is defined by weakly focussing the beam to a focal area of about 1 mm^2. Calorimeter and vidicon measurements[2] performed for each laser shot provide the peak fluence level at the center of the approximately Gaussian beam profile.

Before data are collected for a new spot on the target, it is first illuminated by several laser shots at a fluence level of about 1/4 - 1/2 of the damage threshold. A large charge emission and a burst of pressure in the chamber are observed during the first one or two shots, presumably caused by the desorption of contaminants from the surface. Subsequent recontamination of the surface is negligible, since the time of formation of an adsorbed monolayer at $\sim 10^{-10}$ Torr is much longer than the three minute interval between shots. After the cleaning shots, charge emission is a reproducible function of fluence level, even for different cleaned spots on the sample.

Some typical logarithmic plots of total collected charge versus fluence level at a pulsewidth of 1 nsec are shown in Fig. 1 for photon energies $h\nu$ = 1.16 eV and 3.5 eV. Each experimental point corresponds to one laser shot. The collected charge was negative and nearly constant in magnitude for a given fluence, for collector potentials from zero to + 300 V. The data of Fig. 1 were therefore obtained with collector potentials of 0 - 10 volts in order to eliminate drifts caused by collection of stray charges in the vacuum system. The results obtained with a negative collector bias varied from sample to sample. In most cases, no positive charge was collected at fluence levels well below the damage threshold. For ZnS and SiO_2 samples, however, we observed nearly equal negative and positive emission with positive and negative collector biases, respectively. This aspect of the photoemission process and also the possibility of neutral atom emission,[3] warrant further investigation. For materials of moderate bandgap, such as CdTe, ZnS, and GeO_2, the charge emission, Q, closely follows a power law dependence on the peak laser fluence F. For wider bandgap materials such as fused silica (SiO_2 in Fig. 1) and NaCl, the very steep slopes and greater scatter in the data give results that are not as definitive, although they are also consistent with such a power law behavior. A distinctive feature of the data is the dependence of the slopes of the curves on the photon energy. In Fig. 3(b), where the photon energy is three times as large as in Fig. 3(a), the slopes are about one-third as large.

In a simple photoemission process involving multiphoton excitation, the emission rate is proportional to $I^N = (F/\tau)^N$, where I is the beam intensity, F is the fluence, τ is the pulsewidth, and N is the smallest integer satisfying $Nh\nu > \Delta E$, where ΔE is the minimum

energy required to promote an electron from the conduction band to the vacuum level. For a rectangular pulse, the total emitted charge is $Q = CF^N/\tau^{N-1}$, where C is a constant for a given sample and pulse duration. The values of N obtained from the slopes of plots such as those in Fig. 1 are given in Table I, and, for both photon energies, they are found to be in agreement with the values calculated assuming that ΔE is the optical bandgap. The apparent insensitivity of N to the work functions given[4] in Table I implies that the excitation of electron-hole pairs is the rate-limiting process. This will be the case, for example, if rapid, linear absorption processes excite the electrons up to the vacuum level once they are produced by the multiphoton absorption.

A lower limit to the mean absorption coefficient for the exciting beam can be estimated from the total emitted charge and an assumed escape depth $\sim 10\text{Å}$ for the electrons. At a flux of 1 GW/cm^2, and $\tau = 1$ nsec, this absorption coefficient ranges from 1 cm^{-1} for CdTe (N=2) and ZnS (N=4) to 10^{-6} cm^{-1} for SiO$_2$ (N=9). Since this estimation assumes a unit escape probability for electrons generated within 10 Å of the surface, the actual absorption coefficients are probably considerably larger. For comparison, a typical interband bulk two-photon absorption coefficient at this flux is in the range 0.1 - 10 cm^{-1}. The intrinsic four-photon and nine-photon absorption coefficients for ZnS and SiO$_2$ would be expected to be many orders of magnitude below the experimentally determined values at the intensities employed in this investigation. With the possible exception of CdTe, therefore, it is

apparent that the charge emission is much larger than would be expected for intrinsic multiphoton absorption. It is, however, possible that the observed emission results from multistep excitation processes involving real intermediate states due to defects, impurities or surface states.

For several of these materials, CdTe, ZnS, CeF_3 and NaCl, data were obtained for two or more pulse durations. Typical results of these measurements for CdTe, ZnS and NaCl are shown in Fig. 2. The simplest way to characterize the results for two different pulselengths is to relate the ratio of fluence levels required to obtain a given magnitude of charge emission to the corresponding ratio of pulse durations. The logarithm of this ratio is given by the horizontal displacement of the curves in Fig. 2. If multiphoton absorption alone is involved in the emission, this ratio would be

$$\frac{F(\tau_1, Q)}{F(\tau_2, Q)} = (\frac{\tau_1}{\tau_2})^{1 - \frac{1}{N}} .$$

For the four materials investigated as a function of pulselength, however, this ratio was close to $(\tau_1/\tau_2)^{1/2}$, although N varied from 2 to 8. The emitted charge therefore increases more rapidly with pulselength than would be expected based solely on multiphoton excitation. This suggests that other processes operate in conjunction with the multiphoton excitation to determine the photoemission yield. Examples of possible additional mechanisms are detrapping of electrons by optical excitation, thereby augmenting diffusion to the surface, or thermally activated diffusion and emission processes.

No sudden increase in the photoemission yield was observed near or above the damage threshold for any of the materials investigated, although such an increase is anticipated if avalanche ionization[5] is involved in the damage process. It is not clear at this time if the mechanisms responsible for the photoemission are also of importance in optical damage. We note, however, that the observed $\tau^{1/2}$ dependence of the fluence required for a given photoemission yield is also found for optical damage thresholds measured on bare polished surfaces with 1064 nm pulses having durations from 0.15 to 20 nsec.[5] Additional measurements of the spatial and temporal behavior and sensitivity to surface conditions of the electron and ion emission are planned in order to investigate their relevance to damage mechanisms.

References

1. See, for example, V. P. Krutyakova and V. N. Smirnov, Sov. Phys. Tech. Phys. <u>24</u>, 1085 (1979) and references therein.

2. W. L. Smith, A. J. DeGroot and M. J. Weber, Appl. Opt. <u>17</u>, 3938 (1978).

3. N. H. Tolk, L. C. Feldman, J. S. Kraus, R. J. Morris, M. M. Traum, and J. C. Tully, Phys. Rev. Lett. <u>46</u>, 134 (1981).

4. Handbook of Thermionic Properties, by V. S. Fomenko, Edited by G. V. Samsonov, Plenum Press Data Division (New York, 1966).

5. For a review of optical damage mechanisms see W. L. Smith, Optical Engineering <u>17</u>, 489 (1978).

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Table 1. Calculated (N_c) and observed (N_{obs}) power law exponents for electron emission from several materials with a range of optical bandgaps (E_g) and work functions (E_w). $h\nu$ is the laser photon energy.

Material	E_g(eV)	E_w(eV)	$h\nu$(eV)	N_c	N_{obs}
CdTe	1.5	6.0	1.16	2	2.1 ± 0.3
NaCl	8.75	4.2	1.16	8	7.2 ± 1.0
SiO$_2$	8.0-8.4	5.0	1.16	7-8	11.0 ± 1.3
			3.5	3	5.0 ± 0.5
ZnS	3.88	5.5	1.16	4	4.4 ± 0.4
			3.5	2	2.1 ± 0.3

Figure Captions

1. Total emitted negative change as a function of fluence level for several materials: (a) $h\nu$ = 1.16 eV, (b) $h\nu$ = 3.5 eV. Numbers in squares are slopes of plotted lines.

2. Total emitted negative charge as a function of fluence level for several pulse lengths for CdTe, ZnS, and NaCl.
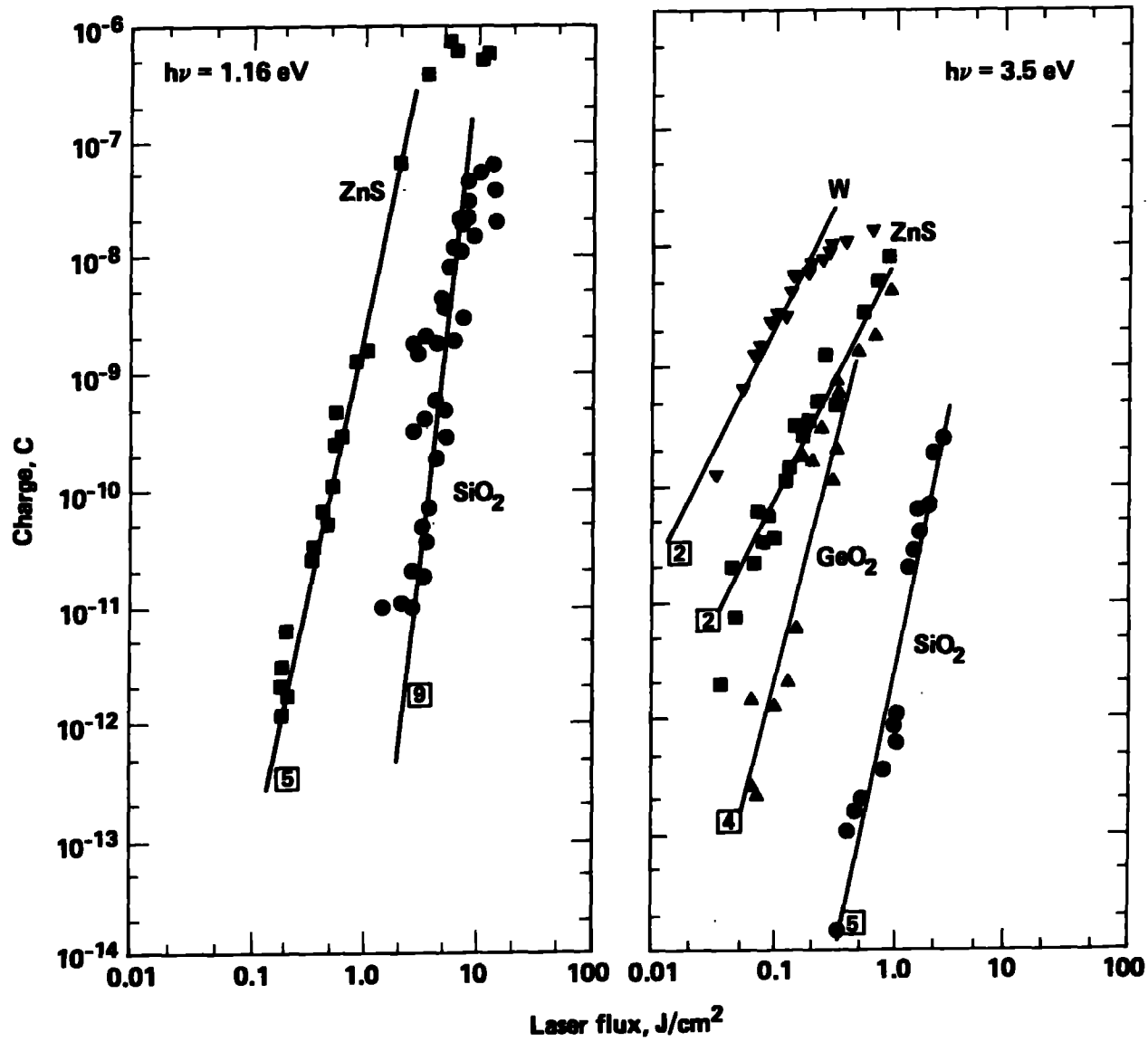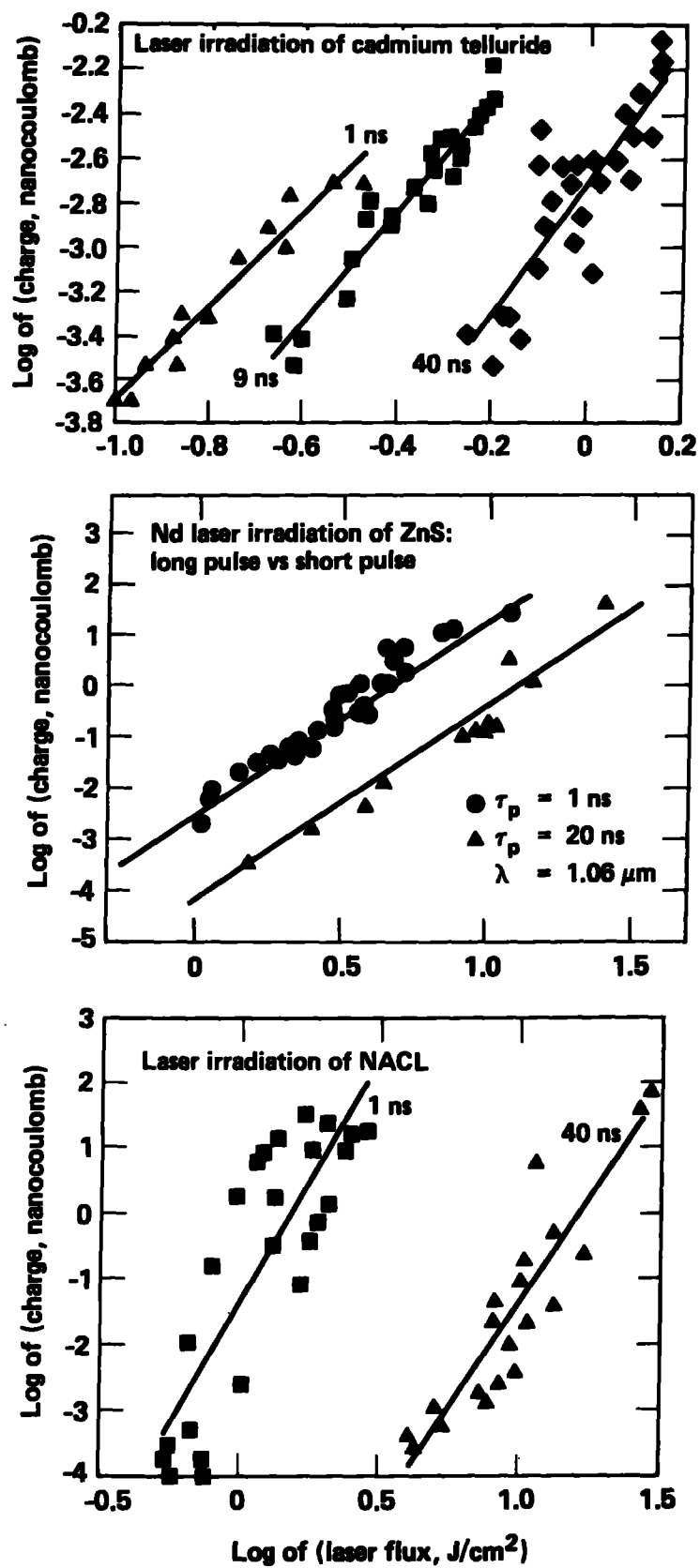
Figure 1

Figure 2